

Stretching of a chain polymer adsorbed at a surface.

J. Krawczyk* and T. Prellberg†

*Institut für Theoretische Physik, Technische Universität Clausthal,
Arnold Sommerfeld Straße 6, D-36578 Clausthal-Zellerfeld, Germany*

A. L. Owczarek‡ and A. Rechnitzer§

*Department of Mathematics and Statistics,
The University of Melbourne, 3010, Australia*

Abstract

In this paper we present simulations of a surface-adsorbed polymer subject to an elongation force. The polymer is modelled by a self-avoiding walk on a regular lattice. It is confined to a half-space by an adsorbing surface with attractions for every vertex of the walk visiting the surface, and the last vertex is pulled perpendicular to the surface by a force. Using the recently proposed flatPERM algorithm, we calculate the phase diagram for a vast range of temperatures and forces. The strength of this algorithm is that it computes the complete density of states from one single simulation. We simulate systems of sizes up to 256 steps.

*Electronic address: krawczyk.jaroslaw@tu-clausthal.de

†Electronic address: thomas.prellberg@tu-clausthal.de

‡Electronic address: aleks@ms.unimelb.edu.au

§Electronic address: andrewr@ms.unimelb.edu.au

I. INTRODUCTION

New experimental methods in the physics of macromolecules [1] have been used to study and manipulate single molecules and their interactions. These methods make a contribution to our understanding of such phenomena as protein folding or unzipping DNA; one can push or pull a single molecule and watch how it responds. It is possible to apply (and measure) forces large enough to induce structural deformation of single molecules. One can monitor the mechanism of some force-driven phase transition occurring at the level of a single molecule. Theoretical understanding of this behaviour has attracted much attention [2, 3, 4]. New features are observed if one pulls a macromolecule localised near an adsorbing surface [5]. One observes two phases: an adsorbed phase and a desorbed phase. The desorbed phase is characterised by the mean fraction of molecules in the adsorbing plane going to zero as the number of molecules in the chain goes to infinity. For a given temperature one can find the critical force at which the macromolecules are desorbed. The phase-diagram in the force-temperature plane can show re-entrant behaviour similar to that found in DNA unzipping models [6] and directed walk models [4].

Lattice models play an important role in the study of equilibrium properties of linear polymer molecules. Including interactions between monomers and a surface confining the polymer, it is possible to investigate phenomena such as the adsorption-desorption transition. The pulling of directed polymers is already well investigated and understood [3, 4]. We use self-avoiding walks (SAW) on a regular lattice to study the adsorption of a polymer at a surface subject to an elongation force. Vrbova and Whittington studied the phase diagram for adsorbing interacting self-avoiding walks using rigorous arguments [5] and simulations with the Markov chain method employing pivot steps [7]. The transition studied by them for polymers in a good solvent (without interaction between monomers) is equivalent to temperature-driven adsorption (without force) in our SAW-model. The model of SAW for force-induced desorption was already investigated by Mishra *et.al.* [8] using exact enumeration, which gave the correct phase diagram but due to the rather small system sizes studied, the location of the phase boundary for infinite systems was not very precise. In this paper we present an investigation of this problem using a new flatPERM algorithm [9]. This is a very good tool to easily get information of the whole phase diagram by calculating the complete density of states. While the exact enumeration study [8] was restricted to $n \leq 19$ steps, flatPERM allowed us to perform “approximate” enumeration up to $n = 256$ steps.

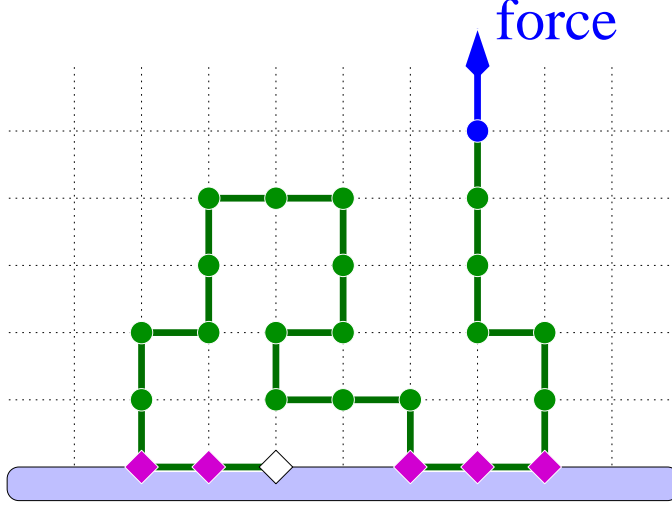


FIG. 1: Example of a configuration near a surface. Monomers interacting with the surface (in two dimensions this is a line) are denoted by diamonds. The first vertex, which is fixed to the surface, is denoted by a white-filled diamond. The elongation force acts only at the last monomer pulling it in the perpendicular direction to the surface.

II. DEFINITION OF THE MODEL

We consider a self-avoiding walk on the simple cubic and square lattices confined to the half-space or half-plane, $z \geq 0$ or $y \geq 0$, respectively. We define a *visit* as a vertex, representing a monomer, lying in the surface $z = 0$ in three dimensions or on the line $y = 0$ in two dimensions. The monomers interact with the surface via an interaction strength, $\epsilon = -1$. In addition we have an elongation force f acting on the last monomer, pulling it away from the surface, i.e. in the positive z -direction or positive y -direction, in three and two dimensions respectively; see Fig. 1. Therefore we have two competing effects: attraction to the surface leading to adsorption and the elongation force leading to desorption. The partition function of the model is given by

$$Z_n(\omega_s, \omega_f) = \sum_{m_s, h} C_{n, m_s, h} \omega_s^{m_s} \omega_h^h, \quad (1)$$

where $C_{n, m_s, h}$ is the number of all configurations with $n + 1$ vertices (monomers) with one end at some fixed origin at the surface $z = 0$ or line $y = 0$, respectively. The number of visits (including the fixed site) is denoted by m_s , and h is the distance of the $(n + 1)$ st vertex from the surface. The Boltzmann weight $\omega_s = e^{-\beta\epsilon} = e^\beta$ ($\epsilon = -1$) is associated with the interaction with the surface and $\omega_h = e^{\beta f}$ with the elongation force f , where $\beta = 1/k_B T$. We define a finite-size free energy $\kappa_n(\omega_s, \omega_h)$ per step as

$$\kappa_n(\omega_s, \omega_h) = \frac{1}{n} \log Z_n(\omega_s, \omega_h). \quad (2)$$

The usual free energy is related to this by $-\beta F_n \equiv n\kappa_n(\omega_s, \omega_h)$. In our simulation we obtain estimates of $C_{n,m_s,h}$, so that a quantity $Q_{n,m_s,h}$ averaged over the set of parameters (m_s, h) for a given length n is calculated by

$$\langle Q \rangle_n(\omega_s, \omega_h) = \frac{\sum_{m_s,h} Q_{n,m_s,h} C_{n,m_s,h} \omega_s^{m_s} \omega_h^h}{\sum_{m_s,h} C_{n,m_s,h} \omega_s^{m_s} \omega_h^h}. \quad (3)$$

In this paper we concentrate on the adsorption and elongation of the self-avoiding walk and the corresponding phase diagram. We investigate the behaviour of the average distance of the last monomer from the adsorbing surface

$$\langle h \rangle = n \frac{\partial \kappa_n}{\partial \log \omega_h}, \quad (4)$$

the average numbers of monomers interacting with the surface

$$\langle m_s \rangle = n \frac{\partial \kappa_n}{\partial \log \omega_s}, \quad (5)$$

and the fluctuations of m_s

$$\sigma^2(m_s) = \langle m_s^2 \rangle - \langle m_s \rangle^2 = n \frac{\partial^2 \kappa_n}{\partial^2 \log \omega_s}. \quad (6)$$

Since the desorption transition is characterised by a significant change in the number of surface adsorbed sites, we also investigate the fluctuations of m_s as a signature of the transition. We are interested in determining the location of the adsorption transition for the whole range of forces and temperatures.

III. ALGORITHM

Since we are interested in investigating the complete phase diagram, one needs to perform simulations for the whole range of temperatures and forces. Conventionally, one would carry out different simulations for numerous values of temperature and force to investigate the region of interest. With the flatPERM algorithm it is possible to cover the whole range (given sufficient time for the simulation to converge) with one single simulation. The flatPERM algorithm is a recently proposed stochastic growth algorithm [9], which performs an estimation of the whole density of states and can be interpreted as an approximate counting algorithm. The algorithm combines the pruned-enriched Rosenbluth method (PERM) [10] with umbrella sampling techniques [11]. The configurations of interest are grown from scratch adding a new monomer at each step. We parameterise the configuration space in such a manner that the algorithm explores it evenly; i.e. for every set of parameters (n, m_s, h) it aims to generate the same number

of samples. This requirement leads to a flat histogram in the parameterisation. Here we choose as parameters the surface energy (number of contacts, m_s) and the distance of the last monomer from the adsorbing surface, h . During one simulation we are able to explore all possible sets of parameters (all vectors (n, m_s, h) for all $n \leq 256$) and estimate the associated density of states $C_{n, m_s, h}$. As an example, for $n = 256$ we have calculated a histogram over 33151 vectors for both dimensions.

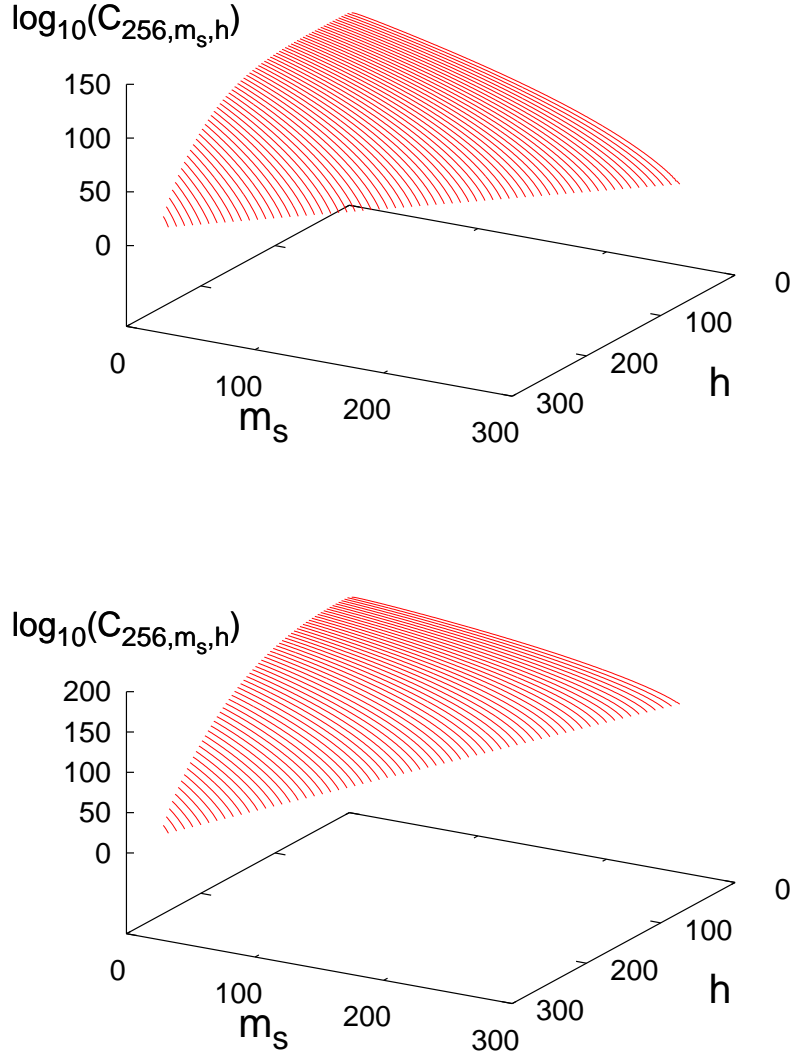


FIG. 2: Density of states for $n = 256$ in two (top) and three (bottom) dimensions. The weights of all vectors $(256, m_s, h)$ were found during one simulation with flatPERM.

IV. RESULTS

In this section we present the results for both two and three dimensions. Fig. 2 shows the density of states for two and three dimensions for polymers of length $n = 256$ steps. From this we can calculate all quantities of interest using eqn. (3). Because we are focusing on the transition between desorbed and adsorbed phases we consider the changes in both m_s and h .

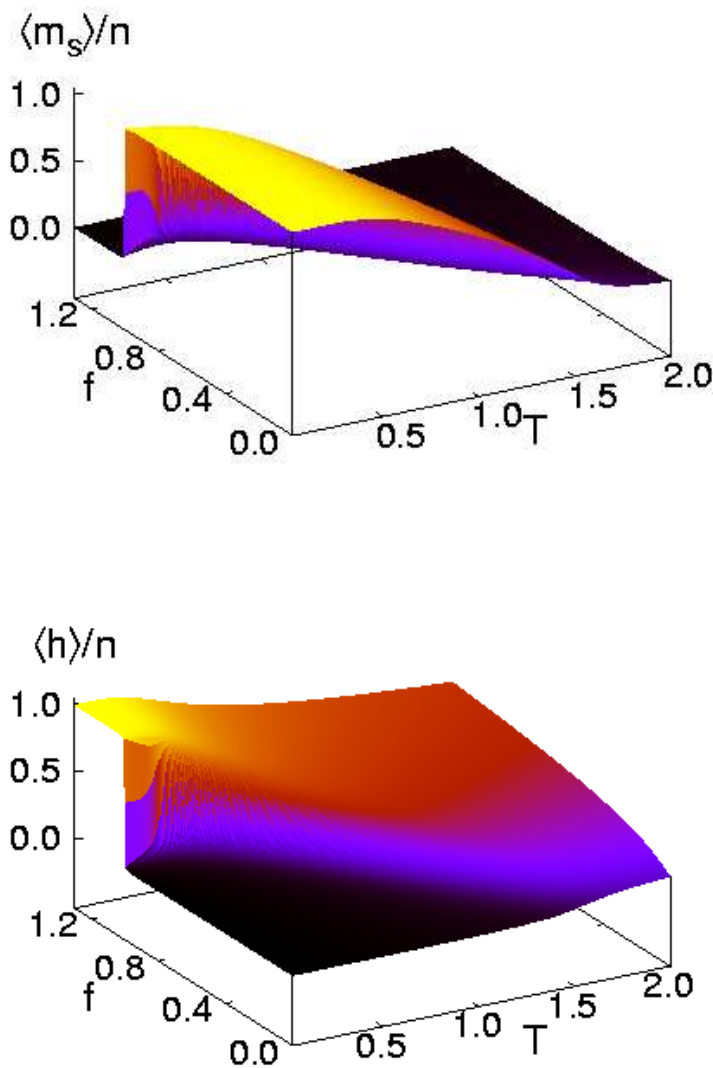


FIG. 3: The average number of surface contacts m_s (top) and the average height per monomer h/n (bottom) in two dimensions at length $n = 256$. One can see two well-distinct phases. The desorbed phase is characterised by $h > 0$ and $m_s \approx 1$. For the adsorbed phase m_s reaches its maximal value while $h \approx 0$. If the force is bigger than one the system is desorbed for all temperatures.

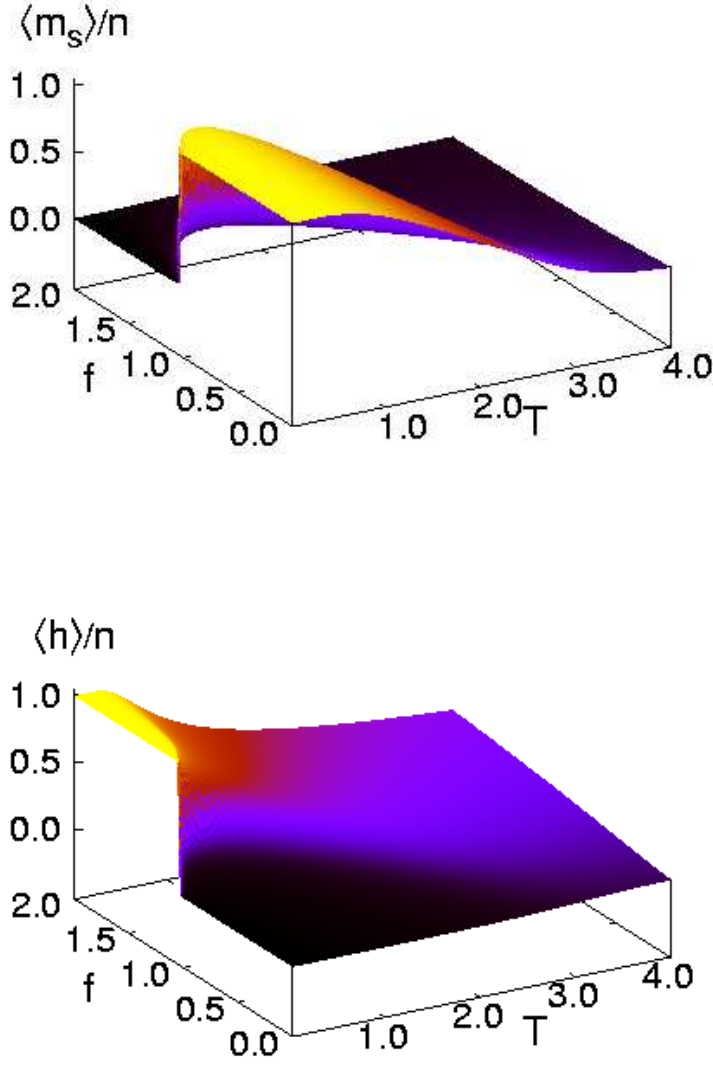


FIG. 4: The average number of surface contacts m_s (top) and the average height per monomer h/n (bottom) in three dimensions at length $n = 256$. For values of force $f < 1$ the behaviour of the system is similar to the two-dimensional case moving from a desorbed phase at low temperatures to a desorbed phase for high temperatures. Above the critical force $f = 1$ re-entrant behaviour occurs up to some maximum force f_{max} . For some force f , with $f_{max} \geq f > 1$, the system moves from the desorbed to adsorbed and back to the desorbed phase as the temperature is increased from near zero.

At low temperatures we find, for both dimensions, a clear indication of a desorption transition between an adsorbed state in which the average number of surface contact is maximal ($m_s \approx n$) to an elongated desorbed state in which the polymer is completely stretched ($h \approx n$) and pulled away from the surface. For higher temperatures this transition persists up to a critical

temperature, at which thermal fluctuations alone lead to desorption. In Fig. 3 one can see the behaviour of the average number of visits m_s and the average distance h of the last vertex from the adsorbing surface for two dimensions, $n = 256$. For forces $f > 1$ in two dimensions the system is desorbed for all temperatures. In three dimensions, Fig. 4 shows that the behaviour is similar but not identical. Here we see the re-entrant behaviour previously observed in directed models [4]. For a range of forces $f > 1$, though not too large, if one fixes the force and considers going from small to high temperatures the system is first desorbed then at some temperature depending on the force becomes adsorbed, and after further increasing the temperature further the system becomes once again desorbed. Such behaviour does not appear in two dimensions.

We estimate the phase boundary looking for positions of maximal fluctuations in m_s . The fluctuations in m_s for $n = 256$ are shown for both dimensions in Fig. 5. The fluctuations separate two distinct phases (the adsorbed phase and the desorbed phase). The whole phase diagram for three different sizes of the system is shown in Fig. 6.

There is a simple approximate argument to understand the difference between both models (the existence of re-entrance in three dimensions), for details see e.g. [4, 8]. Using this argument one finds that for T close to zero in the d -dimensional system the critical force is given by

$$f_c^{(d)} \approx -\epsilon + T \cdot \log \mu_{d-1} = 1 + T \cdot \log \mu_{d-1}, \quad (7)$$

where μ_{d-1} is the connective constant in $d - 1$ dimensions. The interesting region of the phase diagram is shown in Fig. 7. Since for two dimensions the entropy for small T is equal to zero (there are only two configurations contributing at $T = 0$) we see that the critical force is equal to one. In three dimensions the entropy for small T is equal to the conformational entropy of self-avoiding walk in two dimensions of length m_s . By fitting the relation of eqn. (7) we find that $\log \mu_2 \approx 0.965$. Given our small system size, this is in reasonable agreement with the established value of the connective constant for SAW in two dimensions $\log \mu_2 \approx 0.97008 \dots$ [17].

If we do not apply any force we have a transition which is driven only by temperature. The position of this transition depends on n and the estimates are only approximations of the phase transition location in the thermodynamic limit. With increasing n , the position of the transition approaches, of course, the real thermodynamic location. In Fig. 8 we estimate the transition temperature for infinite systems using the value of the cross-over exponent obtained by Grassberger and Hegger [15] $\phi = 1/2$. We see that the corrections to finite-size scaling are stronger than linear for both dimensions. Fitting a simple quadratic function to our data we find the values $T = 1.71$ for two dimensions and $T = 3.27$ for three dimensions. The transition

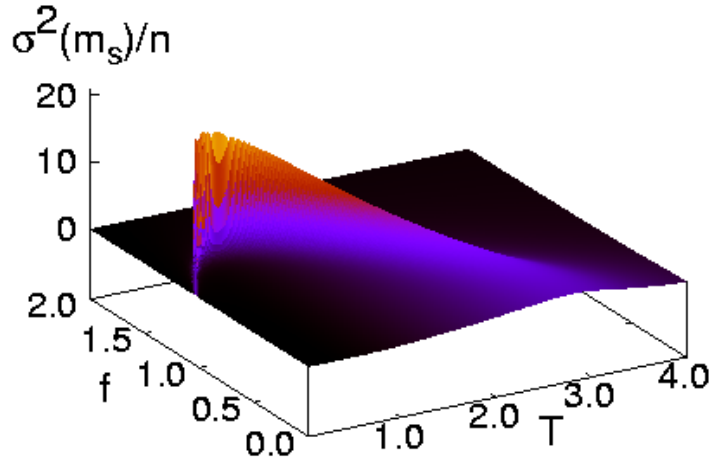
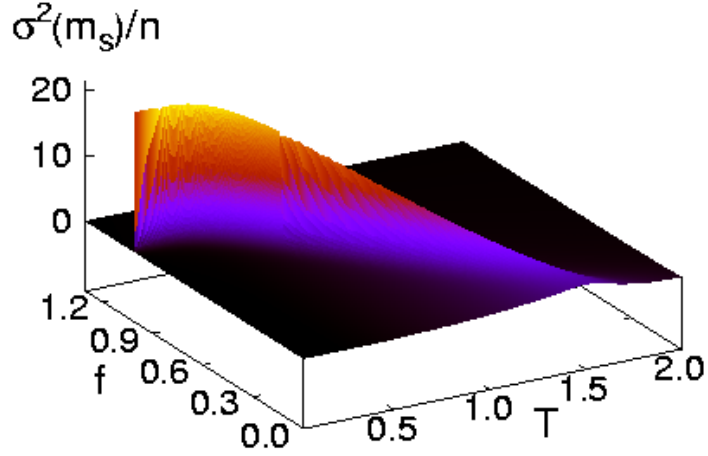


FIG. 5: Fluctuations of m_s in two (left) and three (right) dimensions for $n = 256$. One can distinguish two different phases (an adsorbed phase and a desorbed phase), which are separated by a peak in the fluctuations.

temperature for three dimensions is smaller than the value found by Vrbova and Prochazka in [16] ($T = 3.39(2)$) based on simulations of systems of size up to $n = 1600$.

V. CONCLUSION

We have presented an application of the flatPERM algorithm to a simple desorption problem with an intriguing phase-diagram that mimics that expected for DNA unzipping models. Using

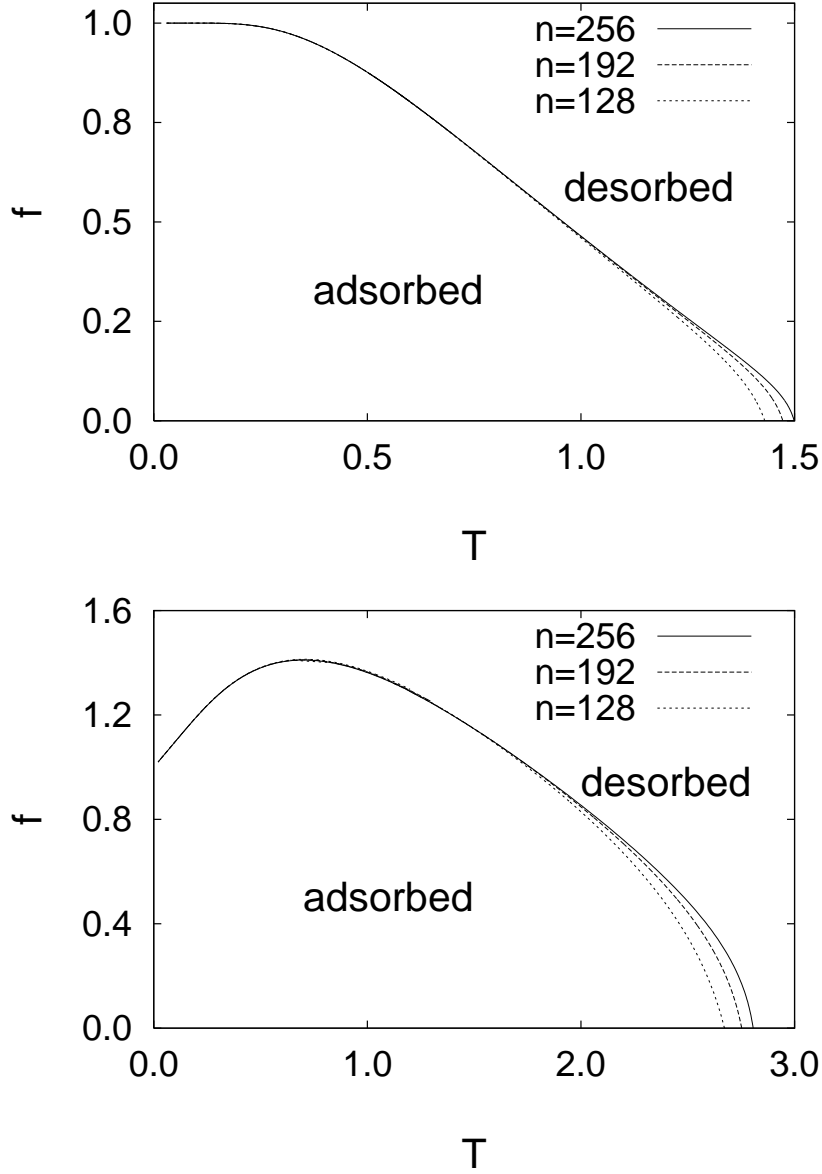


FIG. 6: Phase diagram for three different lengths for two (top) and three (bottom) dimensions. One can clearly see the difference between the systems. In three dimensions we have clear re-entrant behaviour. There is no difference in the transition position for small temperature and high force, while for higher temperature and small force the position of the transition depends on the system size n .

flatPERM one may quickly get a good qualitative overview of the whole phase diagram. In further studies we extend our simulations to investigations of adsorption of interacting self-avoiding walks at a surface, where we have found intriguing and novel phenomena [18, 19].

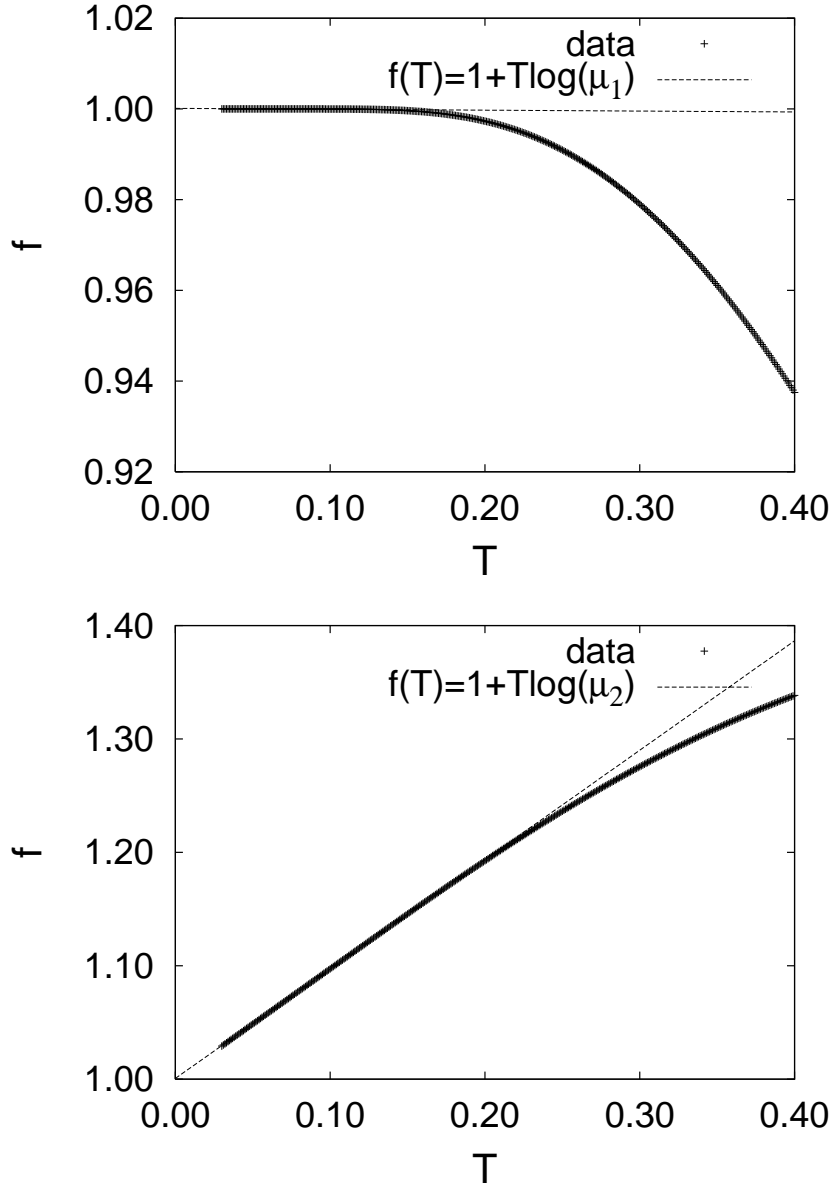


FIG. 7: The critical force for $T \rightarrow 0$ is found to fulfill the relation $f(T) = 1 + T \cdot \log \mu_{d-1}$ for both two dimensions (top) and three dimensions (bottom). The respective surface connective constants are $\log \mu_2 \approx 0.965$ and $\log \mu_1 = 0$. The solid line is the data from our simulations and the dashed line is the relation.

Acknowledgements

Financial support from the DFG is gratefully acknowledged by JK and TP. Financial support from the Australian Research Council is gratefully acknowledged by ALO and AR. ALO also

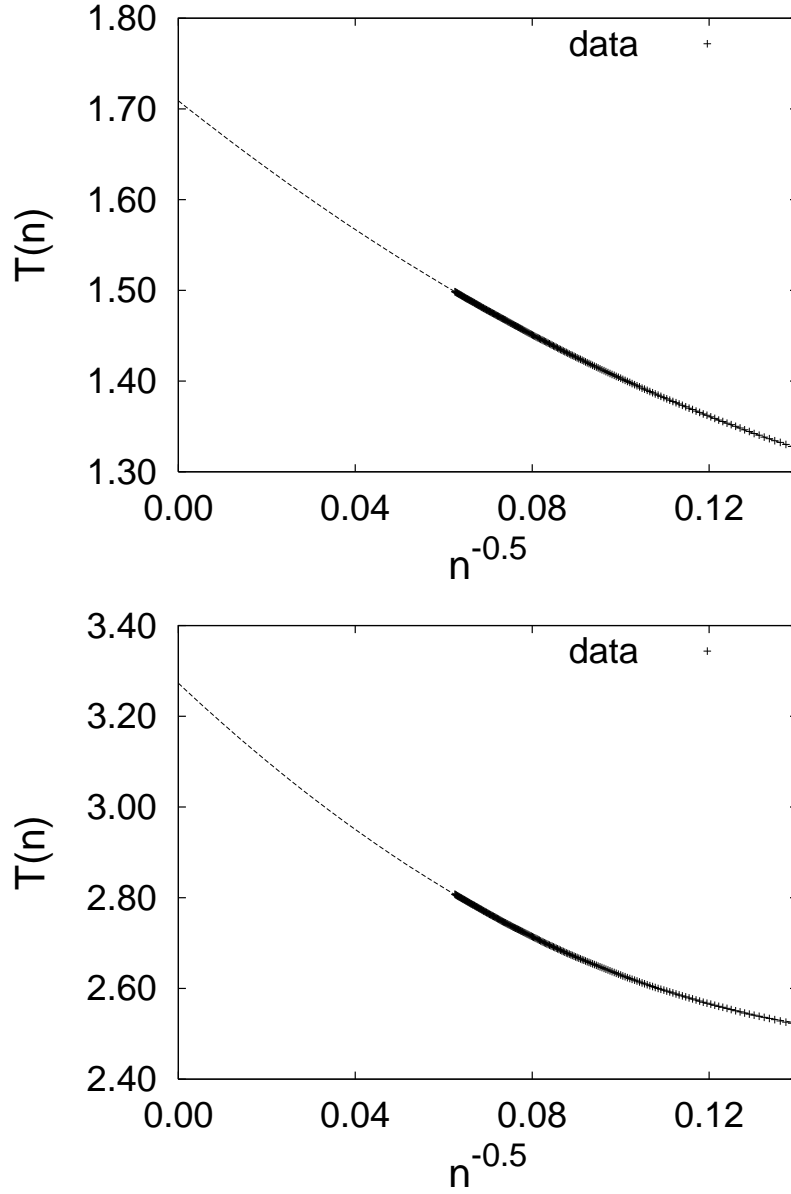


FIG. 8: The transition temperature between adsorbed and desorbed phase in the absence of force ($f = 0$) for two (top) and three (bottom) dimensions. The solid line is our data. We approximate the transition temperature for an infinite system in both dimensions using a least-squares quadratic fit, shown as a dashed line.

thanks the Institut für Theoretische Physik at the Technische Universität Clausthal.

-
- [1] T. Strick, J.-F. Allemand, V. Croquette and D. Bensimon, Phys. Today **54**(10), 46 (2001)
 - [2] D. Marenduzzo, A. Maritan, A. Rosa and F. Seno, Phys. Rev. Lett. **90** 088301 (2003)
 - [3] A. Rosa, D. Marenduzzo, A. Maritan and F. Seno, Phys. Rev. E. **67** 041802 (2003)

- [4] E. Orlandini, M. Tesi and S.G. Whittington, J. Phys. A: Math. Gen. **37** 1535 (2004)
- [5] T. Vrbova and S.G. Whittington, J. Phys. A: Math. Gen. **29** 6253 (1996)
- [6] E. Orlandini, S.M. Bhattacharjee, D. Marenduzzo, A. Maritan and F. Seno, J. Phys. A: Math. Gen. **34** L751 (2001)
- [7] T. Vrbova and S.G. Whittington, J. Phys. A: Math. Gen. **31** 3989 (1998)
- [8] P.K. Mishra, S. Kumar and Y. Singh, e-print cond-mat/0404191
- [9] T. Prellberg and J. Krawczyk, Phys. Rev. Lett. **92** 120602 (2004)
- [10] P. Grassberger, Phys. Rev E **56** 3682 (1997)
- [11] G. M. Torrie and J. P. Valleau, J. Comput. Phys. **23** 187 (1977)
- [12] A. Rechnitzer, J. Krawczyk and T. Prellberg, in preparation
- [13] M. N. Rosenbluth and A. W. Rosenbluth, J. Chem. Phys. **23** 356 (1955)
- [14] H.-P. Hsu, V. Mehra, W. Nadler and P. Grassberger, Phys. Rev. E **68** 21113 (2003)
- [15] P. Grassberger and R. Hegger, Phys. Rev. E **51** 2674 (1995)
- [16] T. Vrbova and K. Prochazka, J. Phys. A **32** 5469 (1999)
- [17] I. Jensen, J. Phys. A: Math. Gen. **37** 5503 (2004)
- [18] A. Owczarek, T. Prellberg, A. Rechnitzer and J. Krawczyk, in preparation
- [19] A. Owczarek, T. Prellberg, A. Rechnitzer and J. Krawczyk, in preparation